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(71) Applicant : TOYO INK MANUFACTURING CO., LTD.
No. 3-13, Kyobashi 2-chome
Chuo-ku
Tokyo (JP)

(72) Inventor : Maki, Hitoshi, c/o Toyo Ink Manufact.Co.Ltd.
3-13, Kyobashi 2-chome, Chuo-ku
Tokyo (JP)
Inventor : Sawamura, Katsuhiko, c/o Toyo Ink Manuf. Co. Ltd.
3-13, Kyobashi 2-chome,
Chuo-ku
Tokyo (JP)
Inventor : Kato, Shigeki, c/o Toyo Ink Manufact.Co.Ltd.
3-13, Kyobashi 2-chome, Chuo-ku
Tokyo (JP)
Inventor : Ikegaya, Toshimitsu, c/o Toyo Ink Manuf. Co. Ltd.
3-13, Kyobashi 2-chome,
Chuo-ku
Tokyo (JP)

(74) Representative : Woods, Geoffrey Corlett
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(54) **Process for the production of copper phthalocyanine pigment and its use.**

(57) A process for the production of a copper phthalocyanine pigment comprising wet-milling at least one of halogen-free, monohalogenated or semi-halogenated copper phthalocyanine in the presence of an inorganic salt as a milling aid and an alcohol or a polyol, and then removing the inorganic salt and the organic liquid,
wherein 0.1 to 20 % by weight, based on the crude copper phthalocyanine, of MePc-$(SO_3^{-}{}^{+}NR_1R_2R_3R_4)_n$ is added before or during the wet-milling, wherein Me represents two hydrogen atoms or at least one metal, Pc is a phthalocyanine residue, each of R_1, R_2, R_3 and R_4 is hydrogen, optionally substituted C_{1-30} alkyl or a polyoxy lower alkylene group and n is 1 to 8, provided that at least one of R_1, R_2, R_3 and R_4 is at least C_{10} or is a polyoxy lower alkylene group.

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Field of the Invention

The present invention relates to a process for the production of a copper phthalocyanine pigment. More specifically, it relates to a process for the production of a copper phthalocyanine pigment, which comprises wet-milling crude copper phthalocyanine in the co-presence of a phthalocyanine derivative, an inorganic salt and an organic liquid. Further, the present invention relates to a printing ink (gravure ink or offset ink) or a coating composition, which has excellent fluidity and excellent gloss and which comprises a copper phthalocyanine pigment obtained by the above process and a vehicle for a printing ink or a vehicle for a coating composition.

Prior Art of the Invention

Finely milled copper phthalocyanine pigments are widely used in large amounts in the industrial field of coloring materials owing to their fine color tones, high tinting strength and excellent properties in weatherability and heat resistance.

Generally, crude copper phthalocyanine is produced by reacting phthalic anhydride or its derivative, urea and a copper source, or reacting phthalodinitrile or its derivative and a copper source, in the presence or absence of a catalyst such as ammonium molybdate or titanium tetrachloride in an organic solvent such as alkylbenzene, trichlorobenzene or nitrobenzene under atmospheric pressure or elevated pressure. During the synthesis of crude copper phthalocyanine, however, synthesized phthalocyanine molecules undergo crystal growth one after another in a synthesis solvent, and it is obtained only in the form of coarse needle-like particles having a major diameter of about 10 to 200 μm. As a consequence, the so-synthesized crude copper phthalocyanine has little or no value as a pigment for coloring an ink, a coating composition and plastics.

Therefore, the above crude copper phthalocyanine is required to be finely milled so that it is converted to particles having high coloring usefulness, i.e., having a particle diameter of approximately 0.01 to 0.5 μm.

For industrially finely milling crude copper phthalocyanine, JP-A-51-28119 typically discloses a so-called solvent-salt milling method in which crude copper phthalocyanine is charged into a double-armed dispersing mixer together with a water-soluble inorganic salt as a milling aid such as sodium chloride and an organic liquid such as an alcohol, a polyol or an amine, and wet-milled. The copper phthalocyanine pigment obtained by the above method has fine particles, and mostly exhibits a high viscosity when dispersed in a vehicle for a gravure ink or a coating composition. It is therefore difficult to take the product out of a dispersing apparatus and transport it. In a worse case, the product sometimes undergoes gelation while it is stored, and can be no longer used. Further, when a different pigment is mixed with the above product, the phenomenons of separation and precipitation induced by aggregation may occur so that nonuniformity in color and a decrease in tinting strength occur in a printed product. Further, a printed or coated surface on the printed product may show a decrease in gloss and defective leveling.

There is another phenomenon involving a change in a crystal state. That is, in a nonaqueous vehicle of an offset ink, a gravure ink or a coating composition, the crystal particles of the pigment, which are unstable with regard to energy, shift to a stable state while altering in size and form. As a result, coarse particles may occur in the vehicle, the hue for a printed product may greatly change, or the tinting strength may decrease. The commercial value of the pigment as a product may therefore be impaired.

For overcoming the above defects, Japanese Patent Publication No. 39-28884, JP-A-52-33922 and JP-A-57-12067 disclose a method in which copper phthalocyanine is mixed with a powder of copper phthalocyaninesulfonic acid organic amine salt having the effect of preventing the crystal growth and aggregation of primary particles. However, a powder of the copper phthalocyaninesulfonic acid organic amine salt itself has high dry-aggregation properties and low dispersibility. For obtaining a sufficient effect by merely mixing copper phthalocyanine with a powder of the above salt, it is required to use a large amount of a powder of the salt.

JP-A-60-133065 discloses a method in which a copper phthalocyaninesulfonic acid amine salt of which the amine salt has 2 to 16 carbon atoms and which has 1 to 2 substituents is added while a crude copper phthalocyanine is wet-milled. However, the above amine salt has a structure of a diamine type, and a copper phthalocyaninesulfonic acid amine salt of this type is ineffective for improving the dispersibility and obtaining a copper phthalocyanine pigment having high tinting strength and a clear hue. That is, a pigment obtained by the above method has problems in practical use, such as a decrease in gloss and color separation induced by aggregation. Further, industrially disadvantageously, the copper phthalocyaninesulfonic acid amine salt of a diamine type requires a very difficult step for its synthesis.

Further, JP-A-60-188470 discloses a method of adding a copper phthalocyanine derivative of which the amine salt has 2 to 8 carbon atoms and which contains a binding group of an alkyl, sulfone or methylcarbonyl group with a copper phthalocyanine, a copper phthalocyanine derivative into which a halogen atom, a nitro group, an amino group, a sulfonic acid group or an alkyl group is directly introduced, or a phthalocyanine of

which the central metal is other than copper. However, this method is still not yet effective for obtaining a copper phthalocyanine pigment having high tinting strength and a clear hue, and a copper phthalocyanine pigment obtained by the above method sometimes has problems in practical use, such as a decrease in gloss and color separation induced by aggregation.

Summary of the Invention

It is an object of the present invention to provide a copper phthalocyanine pigment which gives, when dispersed in a vehicle for a printing ink or a coating composition, printing inks such as a gravure ink and an offset ink and a coating composition all of which have excellent gloss and excellent fluidity.

It is another object of the present invention to provide a printing ink composition comprising a copper phthalocyanine pigment obtained by the above process and a vehicle, and having excellent dispersibility and excellent gloss.

It is further another object of the present invention to provide a coating composition comprising a copper phthalocyanine pigment obtained by the above process and a vehicle, and having excellent dispersibility and excellent gloss.

It is still further another object of the present invention to provide a process for the production of a copper phthalocyanine pigment which exhibits excellent dispersibility and has excellent tinting strength when used for coloring plastics.

According to the present invention, there is provided a process for the production of a copper phthalocyanine pigment, which comprises wet-milling at least one crude copper phthalocyanine selected from the group consisting of halogen-free copper phthalocyanine, a monohalogenated copper phthalocyanine and semi-halogenated copper phthalocyanine in the presence of an inorganic salt as a milling aid and an organic liquid selected from an alcohol and a polyol, and then removing the above inorganic salt and the above organic liquid,

wherein 0.1 to 20 % by weight, based on the crude copper phthalocyanine, of a compound of the following formula (1) is added before or during the wet-milling,

$$MePc - (SO_3^{-+}NR_1R_2R_3R_4)_n \quad (1)$$

wherein Me represents two hydrogen atoms or at least one metal selected from the group consisting of Al, Fe, Co, Ni, Cu and Zn, Pc is a phthalocyanine residue, each of R_1, R_2, R_3 and R_4 is independently a hydrogen atom, an alkyl group having 1 to 30 carbon atoms, a substituted alkyl group having 1 to 30 carbon atoms or a polyoxy lower alkylene group and n is an integer of 1 to 8, provided that at least one of R_1, R_2, R_3 and R_4 is an alkyl group having at least 10 carbon atoms or a polyoxy lower alkylene group.

According to the present invention, further, there is provided a process for the production of a copper phthalocyanine pigment, which comprises wet-milling at least one crude copper phthalocyanine selected from the group consisting of halogen-free copper phthalocyanine, semi-halogenated copper phthalocyanine and monohalogenated copper phthalocyanine in the presence of an inorganic salt as a milling aid and an organic liquid selected from an alcohol and a polyol, and then removing the above inorganic salt and the above organic liquid,

wherein a compound of the above formula (1) is added in an amount of 0.1 to 15 % by weight based on the crude copper phthalocyanine before the wet-milling of the crude copper phthalocyanine is completed and in an amount of 0.1 to 15 % by weight based on the crude copper phthalocyanine after the crude copper phthalocyanine is wet-milled or after the inorganic salt and the organic liquid are removed.

Further, according to the present invention, there is provided a printing ink composition comprising a copper phthalocyanine pigment produced by any one of the above methods and a vehicle.

Further, according to the present invention, there is provided a coating composition comprising a copper phthalocyanine pigment produced by any one of the above methods and a vehicle.

Detailed Description of the Invention

For overcoming the above-described problems, the present inventors have made diligent studies and found the following. When a crude copper phthalocyanine is wet-milled, a phthalocyanine derivative having a different structure from any conventional one is added as an agent for preventing crystal growth and re-aggregation during the wet-milling, whereby the resultant copper phthalocyanine pigment shows excellent fluidity when dispersed in a vehicle for a printing ink or a coating composition and has an excellent clear hue and high tinting strength. On the basis of this finding, the present invention has been completed.

The crude copper phthalocyanine used in the present invention refers to copper phthalocyanines produced by known methods, and is not specially limited. Generally, the crude copper phthalocyanine is produced by reacting phthalic anhydride or its halide, urea and a copper sources, or reacting phthalodinitrile or its halide and a copper source, in the presence or absence of a catalyst such as ammonium molybdate or titanium tet-

rachloride in a solvent such as alkylbenzene, trichlorobenzene or nitrobenzene at a temperature between 120°C and 250°C, preferably between 170°C and 230°C under atmospheric pressure or elevated pressure for 2 to 15 hours, preferably 3 to 7 hours. This crude copper phthalocyanine includes a halogen-free copper phthalocyanine, a monohalogenated copper phthalocyanine containing 1 halogen atom and a semi-halogenated copper phthalocyanine containing 2 to 4 halogen atoms.

In the present invention, a compound of the following formula (1) is added as an agent for preventing crystal growth and aggregation.

$$MePc - (SO_3^{-+}NR_1R_2R_3R_4)_n \quad (1)$$

wherein Me represents two hydrogen atoms or at least one metal selected from the group consisting of Al, Fe, Co, Ni, Cu and Zn, Pc is a phthalocyanine residue, each of R_1, R_2, R_3 and R_4 is independently a hydrogen atom, an alkyl group having 1 to 30 carbon atoms, a substituted alkyl group having 1 to 30 carbon atoms or a polyoxy lower alkylene group and n is an integer of 1 to 8, provided that at least one of R_1, R_2, R_3 and R_4 is an alkyl group having at least 10 carbon atoms or a polyoxy lower alkylene group.

The method for the production of the above compound of the formula (1) is not specially limited, while it can be generally produced by a method in which phthalocyanine is sulfonated by a conventional method and the phthalocyaninesulfonic acid is reacted with an amine component in the presence or absence of a solvent such as water or an organic solvent.

Specific examples of the above amine component include primary amines such as octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, nonadecylamine, eicosylamine, phenylamine and unsaturated amines corresponding to numbers of carbon atoms of these amines (these primary amines may have side chains); and secondary and tertiary amines and quaternary ammonium salts (composed of a combination of an alkyl group forming any one the above primary amines or an aryl group and methyl, ethyl, propyl, butyl or pentyl group) such as dioleylamine, distearylamine, dimethyloctylamine, dimethyldecylamine, dimethyllaurylamine, dimethylstearylamine, dilaurylmonomethylamine, trioctylamine, dimethyldioctylammonium chloride, dimethyldidecylammonium chloride, dimethyldidodecylammonium chloride, dimethyldioleylammonium chloride, trimethylstearylammonium chloride, dimethyldistearylammonium chloride, trimethyldodecylammonium chloride, trimethylhexadecylammonium chloride, trimethyloctadecylammonium chloride, dimethyldodecyltetradecylammonium chloride, and dimethylhexadecyloctadecylammonium chloride.

With an increase in the number of carbon atoms of the alkyl group of the amine component and the number of substituents on the alkyl group, the phthalocyanine derivative shows higher dispersibility. Therefore, the phthalocyanine derivative from such an amine component is effective for obtaining a copper phthalocyanine pigment having high fluidity in a vehicle and gloss.

In the formula (1), any one of R_1, R_2, R_3 and R_4 may be an alkyl group having a substituent. This substituent includes phenyl, halogen, hydroxyl carbonyl, carboxyl, ether, ester and acyl.

In the formula (1), when any one or some of R_1, R_2, R_3 and R_4 represent(s) a polyoxy lower alkylene group, the polyoxy lower alkylene group includes polyoxyethylene and polyoxypropylene. The polyoxy lower alkylene group has a polymerization degree of 2 to 30, preferably 5 to 30.

The amount of the compound of the formula (1) based on the crude copper phthalocyanine is 0.1 to 20 % by weight. When this amount is less than 0.1 % by weight, no effects are obtained. When it exceeds 20 % by weight, uneconomically, no further effect is obtained. The compound of the formula (1) may be added before or during the wet-milling of the crude copper phthalocyanine. Further, the compound of the above formula (1) may be added in an amount of 0.1 to 15 % by weight based on the crude copper phthalocyanine before the wet-milling of the crude copper phthalocyanine is completed and in an amount of 0.1 to 15 % by weight based on the crude copper phthalocyanine after the crude copper phthalocyanine is wet-milled or after the inorganic salt and the organic liquid are removed, whereby there can be obtained a copper phthalocyanine pigment composition having further excellent fluidity.

In the present invention, the crude copper phthalocyanine is wet-milled in the presence of a milling aid selected from inorganic salts and an organic liquid selected from an alcohol and a polyol. The above milling aid includes water-soluble inorganic salts such as sodium chloride, sodium sulfate and calcium chloride. Further, the milling aid is preferably finely milled before use. The amount (weight) of the milling aid is 2 to 10 times, preferably 3 to 8 times, as large as that of the crude copper phthalocyanine.

The organic liquid is preferably one which has solubility in water at least to some extent. It is selected from alcohols and polyols. Examples of the alcohols include as n-propyl alcohol, n-butyl alcohol, isopropyl alcohol and isobutyl alcohol. Examples of the polyols include polyols, ethers of polyols, esters of polyols and chlorinated derivatives of these such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and tetrapropylene glycol. The above organic liquids may be used alone or in combination. The amount (weight) of the organic liquid is 0.1 to 2.0, preferably 0.3 to

1.5, times as large as that of the crude copper phthalocyanine.

The wet-milling apparatus can be selected from various kneaders and mixers used for conventional wet-milling methods.

Although differing depending upon the wet-milling apparatus and the amounts of the milling aid and the organic liquid, the time required for the wet-milling is 1 to 15 hours, preferably 2 to 10 hours. The wet-milling may be carried out longer than 15 hours, while there is no further improvement in the pigment quality, and undesirably, the energy efficiency is deteriorated.

Although differing depending upon the wet-milling apparatus, the amounts of the milling aid and the organic liquid and the milling time, the temperature for the wet-milling is between 20°C and 150°C, preferably between 80°C and 130°C. When the wet-milling temperature is higher than 150°C, the crystal growth occurs sharply, and it is hence required to decrease the wet-milling time. In this case, the time for dressing grains (forming uniform particles) is too short, which is undesirable in view of a product quality. After the wet-milling is initiated, the temperature gradually increases and arrives at an equilibrium at 90 to 120°C, and cooling or heating is effected as required.

The wet-milled copper phthalocyanine pigment is treated by a conventional method. That is, the wet-milled mixture is treated with water or a diluted acid, filtered and washed with water to remove the milling aid and the organic liquid, and the pigment is isolated. The pigment may be used directly in a wet state, or may be used in a powder state after it is dried.

A resin, a surfactant and other additive may be added to the pigment as required.

When a coating composition or a printing ink (gravure ink or offset ink) is produced from the copper phthalocyanine pigment obtained by the process of the present invention, the vehicle therefor is not specially limited. The vehicle may contain an auxiliary and an extender pigment.

The vehicle for the coating composition includes an acrylic resin, an alkyd resin, an epoxy resin, a chlorinated rubber, vinyl chloride, a synthetic resin emulsion, a silicone resin, a polyurethane resin, a polyester resin, a melamine resin, a urea resin, a mixture of at least two of these, and a mixture of a water-soluble resin or an emulsion resin prepared by solubilizing any one of the above resins in water with a solvent such as a hydrocarbon, an alcohol, a ketone, an ether alcohol, an ether, an ester or water.

The vehicle for the gravure ink includes gum rosin, wood rosin, tall oil rosin, lime rosin, rosin ester, a maleic acid resin, a polyamide resin, a vinyl resin, nitrocellulose, cellulose acetate, ethyl cellulose, chlorinated rubber, cyclized rubber, an ethylene-vinyl acetate copolymer resin, a urethane resin, a polyester resin, an alkyd resin, an acrylic resin, gilsonite, dammar, shellac, a mixture of at least two of the above resins, and a mixture of a water-soluble resin or an emulsion resin prepared by solubilizing any one of the above resins in water with a solvent such as a hydrocarbon, an alcohol, a ketone, an ether alcohol, an ether, an ester or water.

The vehicle for the offset ink includes a rosin-modified phenolic resin, a petroleum resin, an alkyd resin, and a mixture of a resin prepared by modifying any one of these resin with an drying oil, a plant oil such as linseed oil, tung oil or soybean oil and a solvent such as n-paraffin, isoparaffin, aromatic, naphthene, α-olefin or water.

The printing ink composition of the present invention and the coating composition of the present invention can be produced by dispersing the above copper phthalocyanine pigment or a mixture of the above copper phthalocyanine pigment with the above phthalocyanine derivative (compound of the formula (1)) in the corresponding vehicle with a dispersing apparatus. The dispersing apparatus is selected from a dissolver, a high speed mixer, a homomixer, a kneader, a flusher, a roll mill, a sand mill and an atriter.

Examples

The present invention will be detailed hereinafter with reference to Examples, in which "part" stands for "part by weight" and "%" stands for "% by weight".

Table 1 shows specific compounds of the formula (1), and Examples refer to numbers of the compounds listed in Table 1.

Table 1

Compound No	Structure
1	$CuPc\text{-}[SO_3{}^{-+}NH_3(C_{12}H_{25})]_1$
2	$CuPc\text{-}[SO_3{}^{-+}NH_3(C_{10}H_{21})]_4$
3	$(Cl)_2\text{-}CuPc\text{-}[SO_3{}^{-+}NH_3(C_{10}H_{21})]_1$
4	$CuPc\text{-}[SO_3{}^{-+}N(CH_3)_2(C_{12}H_{25})_2]_1$
5	$CuPc\text{-}[SO_3{}^{-+}NH_3(C_{12}H_{25})]_3$
6	$CuPc\text{-}[SO_3{}^{-+}N(CH_3)_3(C_{12}H_{25})]_1$
7	$CuPc\text{-}[SO_3{}^{-+}NH(C_{12}H_{25})_3]_2$
8	$FePc\text{-}[SO_3{}^{-+}NH_3(C_{18}H_{35})]_1$
9	$CuPc\text{-}[SO_3{}^{-+}NH_2(C_{12}H_{25})_2]_4$
10	$NiPc\text{-}[SO_3{}^{-+}NH(CH_3)_2(C_{12}H_{25})]_1$
11	$CuPc\text{-}[SO_3{}^{-+}N(CH_3)_2(C_{18}H_{37})_2]_1$
12	$CuPc\text{-}SO_3{}^{-+}N(CH_3)(C_2H_5)_2([CH_2CH(CH_3)O]_{25})H)$
13	$CuPc\text{-}SO_3{}^{-+}N(CH_3)_2(C_{18}H_{37})CH_2\text{-}$⌬
14	$CuPc\text{-}[SO_3{}^{-+}N(C_{18}H_{37})(CH_3)_3)]_2$
15	$(Cl)_8(Br)_2\text{-}CuPc\text{-}[SO_3{}^{-+}NH_2(C_{12}H_{25})_2]_1$
CEx. 12	$CuPc\text{-}[SO_3{}^{-+}NH_3(CH_2)_3N(CH_3)_2]$
CEx. 13	$CuPC\text{-}(CH_2NH\text{-}$⌬$\text{-}CH_3)_2$

CEx. = Comparative Example,

CuPc = copper phthalocyanine residue

FePc = iron phthalocyanine residue

NiPc = nickel phthalocyanine residue

Example 1

100 Parts of a crude halogen-free copper phthalocyanine produced by a conventional method, 400 parts of milled sodium chloride, 80 parts of diethylene glycol and Compounds No. 1 in Table 1 (in an amount shown in Table 2) were charged into a double-armed kneader having a volume of 1,000 parts, and kneaded at 100 to 110°C for 4 hours while maintaining the mixture in the form of a dense mass (dough). Thereafter, the kneaded mixture was added to 1,300 parts of a 1 % sulfuric acid aqueous solution having a temperature of 70°C, and the mixture was stirred under heat at 70°C for 1 hour, filtered, washed with water and dried to give a copper phthalocyanine pigment.

Examples 2 - 5

Copper phthalocyanine pigments were obtained in the same manner as in Example 1 except that Compound No. 1 was replaced with Compounds Nos. 2 to 5 in Table 1 (in amounts shown in Table 2).

Comparative Example 1

A copper phthalocyanine pigment was prepared in the same manner as in Example 1 except that Compound No. 1 was not added.

Comparative Examples 2 - 6

Copper phthalocyanine pigments were prepared in the same manner as in Examples 1 to 5 except that Compounds Nos. 1 to 5 were added when kneaded mixtures were purified with an acid (1 % sulfuric acid aqueous solution).

Examples 6 and 7

100 Parts of a crude, semi-chlorinated copper phthalocyanine prepared by a conventional method, 510 parts of milled sodium chloride, 95 parts of diethylene glycol and one of Compounds Nos. 6 and 7 (for Examples 6 and 7) in Table 1 (in amounts shown in Table 3) were charged into a double-armed kneader having a volume of 1,000 parts, and kneaded at 110 to 120°C for 9 hours while maintaining the mixture in the form of a dense mass (dough). Thereafter, the kneaded mixture was added to 1,500 parts of a 1 % sulfuric acid aqueous solution having a temperature of 70°C, and the mixture was stirred under heat at 70°C for 1.5 hours, filtered, washed with water and dried to give a copper phthalocyanine pigment.

Comparative Example 7

A copper phthalocyanine pigment was prepared in the same manner as in Example 6 except that Compound No. 6 was not added.

Examples 8 - 10

100 Parts of a crude, mono-chlorinated copper phthalocyanine prepared by a conventional method, 550 parts of milled sodium chloride, 80 parts of diethylene glycol and one of Compounds Nos. 8 to 10 (for Examples 8 to 10) in Table 1 (amounts shown in Table 3) were charged into a double-armed kneader having a volume of 1,000 parts, and kneaded at room temperature for 10 hours while maintaining the mixture in the form of a dense mass (dough). Thereafter, the kneaded mixture was added to 1,500 parts of a 1 % sulfuric acid aqueous solution having a temperature of 70°C, and the mixture was stirred under heat at 70°C for 1.5 hours, filtered, washed with water and dried to give a copper phthalocyanine pigment.

Comparative Example 8

A copper phthalocyanine pigment was prepared in the same manner as in Example 8 except that Compound No. 8 was not added.

Examples 11 - 15

100 Parts of a crude, halogen-free copper phthalocyanine prepared by a conventional method, 400 parts of milled sodium chloride, 80 parts of diethylene glycol and one of Compounds Nos. 11 to 15 (for Examples 11 to 15) in Table 1 (amounts shown in Table 4) were charged into a double-armed kneader having a volume of 1,000 parts, and kneaded at 110 to 110°C for 4 hours while maintaining the mixture in the form of a dense mass (dough). Thereafter, the kneaded mixture was added to 1,300 parts of a 1 % sulfuric acid aqueous solution having a temperature of 70°C, and the mixture was stirred under heat at 70°C for 1 hour, filtered, washed with water and dried to give a copper phthalocyanine pigment.

Comparative Example 9

A copper phthalocyanine pigment was prepared in the same manner as in Example 11 except that Compound No. 11 was not added.

Example 16

100 Parts of a crude, halogen-free copper phthalocyanine prepared by a conventional method, 450 parts of milled sodium chloride, 90 parts of diethylene glycol, 4 parts of Compound No. 1 and 3 parts of Compound No. 9 were charged into a double-armed kneader having a volume of 1,000 parts, and kneaded at 110 to 110°C for 5 hours while maintaining the mixture in the form of a dense mass (dough). Thereafter, the kneaded mixture was added to 1,300 parts of a 1 % sulfuric acid aqueous solution having a temperature of 70°C, and the mixture was stirred under heat at 70°C for 1 hour, filtered, washed with water and dried to give a copper phthalocyanine pigment.

Example 17

A copper phthalocyanine pigment was prepared in the same manner as in Example 6 except that the crude, semi-chlorinated copper phthalocyanine was replaced with a crude, halogen-free copper phthalocyanine.

Comparative Example 10

A copper phthalocyanine pigment was prepared in the same manner as in Example 17 except that Compound No. 6 used in Example 17 was not added.

Example 18

A copper phthalocyanine pigment was prepared in the same manner as in Example 8 except that the crude, mono-chlorinated copper phthalocyanine was replaced with a crude, halogen-free copper phthalocyanine.

Comparative Example 11

A copper phthalocyanine pigment was prepared in the same manner as in Example 18 except that Compound No. 8 used in Example 18 was not added.

Example 19

A copper phthalocyanine pigment was prepared in the same manner as in Example 6 except that the crude, semi-chlorinated copper phthalocyanine was replaced with a crude, halogen-free copper phthalocyanine.

Example 20

A copper phthalocyanine pigment was prepared in the same manner as in Example 8 except that the crude, mono-chlorinated copper phthalocyanine was replaced with a crude, halogen-free copper phthalocyanine.

Examples 21 - 25

A copper phthalocyanine pigment was prepared in the same manner as in Examples 1 to 5 except that half of the entire amount of one of Compounds Nos. 1 to 5 was added during the kneading (milling) and that the remaining half was added when the kneaded mixture was purified with an acid (1 % sulfuric acid aqueous solution) after the kneading.

Comparative Example 12

A copper phthalocyanine pigment was prepared in the same manner as in Example 1 except that Compound No. 1 was replaced with Compound No. CEx. 12 shown in Table 1 (described in Example 2 of JP-A-60-133065).

Comparative Example 13

A copper phthalocyanine pigment was prepared in the same manner as in Example 1 except that Compound No. 1 was replaced with Compound No. CEx. 13 shown in Table 1 (described in Example 8 of JP-A-60-188470).

The pigments obtained in Examples 1 to 5, 17, 18 and 21 to 25 and Comparative Examples 1 to 6 and 10 to 13 were evaluated as follows.

20 Parts of one of the above pigments, 80 parts of a gravure ink vehicle composed of components listed below and 300 parts of steal balls were mixed, and the mixture was dispersed with a paint conditioner for 90 minutes to obtain a gravure ink composition. The so-obtained gravure ink composition was measured with a BM viscometer for a fluidity immediately after its preparation and a fluidity (stability with time) after it was allowed to stand at 40°C for 24 hours. Further, the gravure ink composition was color-developed (coated) on a color-developing film and the coating was measured for a gloss with a glossmeter.

(Components for vehicle for gravure ink)	
Nitrocellulose (RS-1/4)	5.5 parts
Ethyl acetate	4.0 parts
Isopropyl alcohol	2.0 parts
Ethyl alcohol	20.0 parts
Plasticizer	1.0 part

Table 2

	Pigment composition Pigment	Compound No.	Amount	Fluidity (cps) BM viscometer Value at 6 rpm A1*	A2*	Gloss
Ex.1	C.I. Pigment Blue 15:3	1	8 %	3,700	12,400	78 %
Ex.21	ditto	1	8 %	2,400	9,000	81 %
CEx.1	ditto	-	-	5,600	30,100	60 %
CEx.2	ditto	1	8 %	4,800	18,600	68 %
CEx.12	ditto	CEx.12	8 %	5,400	29,600	62 %
CEx.13	ditto	CEx.13	8 %	4,700	34,300	70 %
Ex.2	ditto	2	10 %	3,200	10,800	81 %
Ex.22	ditto	2	10 %	2,050	8,400	84 %
CEx.3	ditto	2	10 %	4,200	16,400	74 %
Ex.3	ditto	3	6 %	3,800	11,800	78 %
Ex.23	ditto	3	6 %	3,000	10,000	80 %
CEx.4	ditto	3	6 %	4,400	14,400	69 %
Ex.4	ditto	4	10 %	3,000	9,400	80 %
Ex.24	ditto	4	10 %	1,950	7,200	85 %
CEx.5	ditto	4	10 %	4,200	12,400	75 %
Ex.5	ditto	5	18 %	2,500	7,800	81 %
Ex.25	ditto	5	18 %	1,430	4,380	84 %
CEx.6	ditto	5	18 %	4,800	10,200	76 %
Ex.17	C.I. Pigment Blue 15:1	2	10 %	3,400	11,500	79 %
CEx.10	ditto	-	-	6,700	29,600	64 %
Ex.18	ditto	3	6 %	4,200	12,800	78 %
CEx.11	ditto	-	-	6,300	32,000	60 %

Ex. = Example, CEx. = Comparative Example
A1: = Fluidity immediately after preparation (dispersion)
A2: = Fluidity after composition was allowed to stand at 40°C for 24 hours.

The pigments obtained in Examples 6 to 10 and Comparative Examples 7 and 8 were evaluated as follows.

20 Parts of one of the above pigments, 60 parts of a coating composition vehicle composed of components listed below and 300 parts of steal balls were mixed, and the mixture was dispersed with a paint conditioner for 90 minutes. Then, 33.8 parts of an alkyd resin varnish and 14.5 parts of a melamine resin varnish were added to the dispersion to obtain a coating composition. The coating composition was measured for a fluidity with a BM viscometer immediately after its preparation. The coating composition was color-developed (coated) and the coating was measured for a gloss with a glossmeter.

(Components for vehicle for coating composition)

Alkyd resin varnish (nonvolatile content 60 %)
26.4 parts
Melamine resin varnish (nonvolatile content 50 %) Suwazole (solvent, supplied by Nihon Sekiyu Co.)
20.0 parts

Table 3 shows the results.

Table 3

	Pigment composition: Pigment	Compound No.	Amount	Fluidity (cps) BM viscometer Value at 6 rpm A1*	A2*	Gloss
Ex.6	C.I. Pigment Blue 15:1	6	7 %	6,400	10,020	88 %
Ex.7	ditto	7	7 %	7,700	11,500	84 %
CEx.7	ditto	-	-	8,700	12,600	73 %
Ex.8	ditto	8	7 %	7,300	11,300	83 %
Ex.9	ditto	9	4 %	6,800	9,800	88 %
Ex.10	ditto	10	4 %	7,400	11,000	86 %
CEx.8	ditto	-	- %	8,800	13,400	75 %
Ex.19	C.I. Pigment Blue 15:3	6	7 %	4,800	6,600	92 %
Ex.20	ditto	8	7 %	5,300	7,400	90 %

Ex. = Example, CEx. = Comparative Example
A1: = Fluidity immediately after preparation (dispersion)
A2: = Fluidity after composition was allowed to stand at 40°C for 24 hours.

The pigments obtained in Examples 11 to 16 and Comparative Example 9 were evaluated as follows.

17 Parts of one of the above pigments and 76 parts of a rosin-modified phenolic resin varnish (nonvolatile content 70 %) were mixed, and the mixture was kneaded with a three-roll mill. Then, the kneaded mixture was adjusted to a tack of 9.0 to 9.5 by adding a petroleum solvent to give an offset ink composition. The so-obtained composition was measured for a fluidity immediately with a spreadometer after it was prepared. Further, the composition was color-developed and measured for a gloss with a glossmeter and for a tinting strength with a densitometer.

Table 4 shows the results.

Table 4

	Pigment composition: Pigment	Compound No.	Amount	Fluidity SR	Slope	Density of proof printing 0.2 cc	Gloss (%)
Ex.11	C.I. Pigment Blue 15:3	11	8 %	18.4	4.7	2.02	67
Ex.12	ditto	12	8 %	18.2	4.4	2.03	68
Ex.13	ditto	13	5 %	17.9	4.4	1.98	62
Ex.14	ditto	14	5 %	18.0	4.2	1.99	65
Ex.15	ditto	15	5 %	17.9	4.0	2.10	66
Ex.16	ditto	1	4 %	18.2	4.0	2.02	66
		9	4 %				
CEx.9	ditto	-	-	17.4	3.9	1.82	61

The above results show the following. The printing ink and the coating composition containing the pigment produced by the process of the present invention shows excellent fluidity and gives a printed product or coating having excellent gloss as compared with the printing ink and the coating composition obtained from a phthalocyanine pigment alone or by dry-blending a phthalocyanine pigment and a phthalocyanine derivative.

When the pigment produced by the process of the present invention is dispersed in a vehicle for a printing ink or a coating composition, the resultant dispersion remarkably shows excellent fluidity over a conventional composition containing pigment alone or a dry blend of a pigment and a phthalocyanine derivative. Further, a color-developed product or a coating obtained from a printing ink or a coating composition containing the pigment produced by the process of the present invention shows improved gloss. Further, when the pigment produced by the process of the present invention is used for coloring plastics, the pigment shows excellent fluidity and gives a colored product having high tinting strength.

In formula (1), when R_1, R_2, R_3 and R_4 is a polyoxy lower alkylene group, the alkylene group preferably comprises from 1 to 4 carbon atoms. Preferred examples of suitable polyoxy lower alkylene groups include polyoxyethylene and polyoxypropylene.

The inorganic salt used in the process of the invention is any inorganic salt conventionally used as a milling aid. The salt is preferably water-soluble. Suitable salts include salts of sodium, calcium and magnesium. The salts may be chlorides, bromides or sulphates. Preferred examples of suitable salts are sodium chloride, sodium sulphate and calcium chloride.

The organic liquid used in the process of the invention is selected from alcohols and polyols. The liquid is preferably soluble in water at least to some extent. Suitable alcohols are C_{1-8} alcohols, preferably C_{1-4} alcohols. Examples include n-propyl alcohol, n-butyl alcohol, isopropyl alcohol and isobutyl alcohol. Suitable polyols include polyols, ethers of polyols, esters of polyols, and chlorinated derivatives thereof. Preferred are polyols having 2 to 15 carbon atoms, preferably 2 to 12 carbon atoms. Suitable examples include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and tetrapropylene glycol.

Claims

1. A process for the production of a copper phthalocyanine pigment, which comprises wet-milling at least one crude copper phthalocyanine selected from halogen-free copper phthalocyanine, monohalogenated copper phthalocyanine and semi-halogenated copper phthalocyanine in the presence of an inorganic salt as a milling aid and an organic liquid selected from an alcohol and a polyol, and then removing the inorganic salt and the organic liquid,

   wherein 0.1 to 20 % by weight, based on the crude copper phthalocyanine, of a compound of the following formula (I) is added before or during the wet-milling,

   $$MePc - (SO_3^{-+}NR_1R_2R_3R_4)_n \quad (1)$$

   wherein Me represents two hydrogen atoms or at least one metal selected from Al, Fe, Co, Ni, Cu and Zn, Pc is a phthalocyanine residue,each of R_1, R_2, R_3 and R_4 is independently a hydrogen atom, an optionally substituted alkyl group having 1 to 30 carbon atoms or a polyoxy lower alkylene group and n is an integer of 1 to 8, provided that at least one of R_1, R_2, R_3 and R_4 is an alkyl group having at least 10 carbon atoms or a polyoxy lower alkylene group.

2. A process according to claim 1, wherein a compound of the above formula (1) is added in an amount of 0.1 to 15 % by weight based on the crude copper phthalocyanine before the wet-milling of the crude copper phthalocyanine is completed and in an amount of 0.1 to 15 % by weight based on the crude copper phthalocyanine after the crude copper phthalocyanine is wet-milled or after the inorganic salt and the organic liquid are removed.

3. A process according to claim 1 or 2, wherein a compound obtained by sulfonating a phthalocyanine and reacting the sulfonated phthalocyanine with an amine is used as the compound of the formula (1).

4. A process according to claim 3, wherein the amine is at least one selected from primary, secondary and tertiary amines and quaternary ammonium.

5. A process according to any preceding claim, wherein the alkyl group is substituted with at least one of phenyl, halogen, hydroxyl, carbonyl, carboxyl, ether, ester and acyl.

6. A process according to any preceding claim, wherein the polyoxy lower alkylene group has a polymerization degree of 2 to 30.

7. A process according to any preceding claim, wherein the milling aid is a water-soluble inorganic salt.

8. A process according to any preceding claim, wherein the organic liquid is water-soluble.

9. A printing ink composition comprising the pigment according to any one of claims 1 to 8 and a vehicle.

10. A coating composition comprising the pigment according to any one of claims 1 to 8 and a vehicle.

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(71) Applicant : **TOYO INK MANUFACTURING CO., LTD.**
No. 3-13, Kyobashi 2-chome
Chuo-ku
Tokyo (JP)

(72) Inventor : **Maki, Hitoshi, c/o Toyo Ink Manufact.Co.Ltd.**
3-13, Kyobashi 2-chome, Chuo-ku
Tokyo (JP)
Inventor : **Sawamura, Katsuhiko, c/o Toyo Ink Manuf. Co. Ltd.**
3-13, Kyobashi 2-chome,
Chuo-ku
Tokyo (JP)
Inventor : **Kato, Shigeki, c/o Toyo Ink Manufact.Co.Ltd.**
3-13, Kyobashi 2-chome, Chuo-ku
Tokyo (JP)
Inventor : **Ikegaya, Toshimitsu, c/o Toyo Ink Manuf. Co. Ltd.**
3-13, Kyobashi 2-chome,
Chuo-ku
Tokyo (JP)

(74) Representative : **Woods, Geoffrey Corlett**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(54) **Process for the production of copper phthalocyanine pigment and its use.**

(57) A process for the production of a copper phthalocyanine pigment comprising wet-milling at least one of halogen-free, monohalogenated or semi-halogenated copper phthalocyanine in the presence of an inorganic salt as a milling aid and an alcohol or a polyol, and then removing the inorganic salt and the organic liquid, wherein 0.1 to 20 % by weight, based on the crude copper phthalocyanine, of MePc-$(SO_3^{-}{}^{+}NR_1R_2R_3R_4)_n$ is added before or during the wet-milling, wherein Me represents two hydrogen atoms or at least one metal, Pc is a phthalocyanine residue, each of R_1, R_2, R_3 and R_4 is hydrogen, optionally substituted C_{1-30} alkyl or a polyoxy lower alkylene group and n is 1 to 8, provided that at least one of R_1, R_2, R_3 and R_4 is at least C_{10} or is a polyoxy lower alkylene group.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	FR-A-2 384 000 (CIBA GEIGY AG) 13 October 1978 * page 2, line 17 - page 3, line 26 * ---	1-10	C09B67/04 C09B67/22 C09D11/02 C09D7/12
D,Y	DATABASE WPI Section Ch, Week 8534 Derwent Publications Ltd., London, GB; Class A25, AN 85-207835 & JP-A-60 133 065 (DAINIPPON INK CHEM KK) , 16 July 1985 * abstract * ---	1-10	
D,A	DATABASE WPI Section Ch, Week 8209 Derwent Publications Ltd., London, GB; Class A60, AN 82-16611E & JP-A-57 012 067 (TOYO INK MFG KK) , 21 January 1982 * abstract * ---	1-10	
A	FR-A-2 128 493 (AMERICAN CYANAMID CO.) 20 October 1972 * page 1, line 15 - page 4, line 22 * ---	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C09B C09D
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 August 1995	Dauksch, H

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